FINAL REPORT

IMPACTS OF SPATIO-VARIABILITY OF SOURCE MORPHOLOGY ON

FIELD-SCALE PREDICTIONS OF SUBSURFACE CONTAMINANT TRANSPORT

August 1, 1998

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REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, includ~~~~ ~~ta sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Se~~~~ pect of the collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE August 1, 1998	3. REPORT TYPE AND DATE COVERED Final Report 04/15/95 - 07/14/98

4. TITLE AND SUBTITLE Impacts of Spatio-Variability of Source Morphology on Field-Scale Predictions of Subsurface Contaminant Transport	5. FUNDING NUMBERS F49620-95-1-0321
6. AUTHOR(S) Kirk Hatfield, Wendy D. Graham, Michael D. Annable, P.S.C. Rao	

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Florida 219 Grinter Hall P.O. Box 115500 Gainesville, FL 32611	8. PERFORMING ORGANIZATION REPORT NUMBER Final Report

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NA 110 Duncan Ave, Rm B115 Bolling AFB DC 20332-8050 AFOSR/JA 110 Duncan Ave, Rm 114 Bolling AFB DC 20332-8050	10. SPONSORING/MONITORING AGENCY REPORT NUMBER Final Report

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT **DISTRIBUTION STATEMENT A** Approved for Public Release Distribution Unlimited	12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 Words)
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14. SUBJECT TERMS		15. NUMBER OF PAGES 37
		16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

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ABSTRACT

This research project investigated the coupled effects of uncertain contaminant source morphology (organic immiscible liquids distribution and composition) and aquifer properties on predicting solute transport in saturated groundwater systems contaminated with residual Organic Immiscible Liquids (OIL's). Research efforts focused on the development of multiple stochastic inverse models for characterizing contaminant fluxes in the near field and for characterizing NAPL distributions within the source. In addition, work was conducted on the forward stochastic modeling, that is, to evaluate individual and collective impacts of uncertain spatially and temporally variable source morphological characteristics on subsurface solute transport predictions. The study also involved 1-, 2-, and 3-dimensional experimental efforts to study bench-scale and intermediate-scale uncertainties associated with OIL sources. These studies focussed on describing dissolution from multi-component OIL's at varying residual fluid saturations and distributions, and the characterization of OIL sources using partitioning and interfacial tracers. As a final component of the project, the various stochastic models developed were evaluated using data from the pilot-scale field experiments conducted at Hill AFB, Columbus AFB, and Base Borden, Ontario, Canada. Data derived from partitioning/interfacial tracers and far-field dissolved OIL component distributions were used with the stochastic models to characterize OIL sources at each site.

INTRODUCTION

The goal of this research project was to investigate the coupled effects of uncertain contaminant source morphology (organic immiscible liquids distribution and composition) and aquifer properties on predicting solute transport in saturated groundwater systems contaminated with residual Organic Immiscible Liquids (OIL's). To achieve this goal, research was conducted to complete the following specific objectives:

1) Investigate how variations in source morphology (OIL distribution and composition) impact variations in aqueous phase concentrations and fluxes over time and space occurring in both the contaminant source region (the near-field zone) and in regions down gradient (the far-field zone) within the contaminant plume;

2) Examine the feasibility and quantify the uncertainty of using effective spatially- and temporally-averaged processes and parameters to predict near- and far-field contaminant movement in heterogeneous groundwater systems; and

3) Investigate the feasibility of reducing contaminant transport prediction uncertainty using site-specific point observations of a heterogeneous groundwater system.

The above research objectives were pursued by conducting three primary tasks which involve stochastic modeling and laboratory experiments.

Task I of the project involved development of stochastic models which incorporate the effects of source characteristic uncertainty (including location, mass, and composition) in addition to uncertain aquifer characteristics (such as hydraulic conductivity, sorption characteristics) that have traditionally been considered. Research efforts focused on the development of stochastic inverse models for characterizing contaminant fluxes in the near field and for characterizing NAPL distributions within the source. In addition, work was conducted on the forward stochastic modeling, that is, to evaluate individual and collec-

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tive impacts of uncertain spatially and temporally variable source morphological characteristics on subsurface solute transport predictions. Under Task I, stochastic modeling was conducted over three broad areas: a first set of models was developed to characterize the near-field region or source zone (contaminant source distribution and aquifer properties) using partitioning and/or interfacial tracer test results. A second set of inverse models was developed to make use of far-field aqueous phase contaminant concentration data to locate sources or define contaminant fluxes at arbitrary downstream source planes. Finally, a third set of models was developed to predict dissolution and far-field contaminant transport in heterogeneous groundwater systems given the aquifer and stochastic source zone characterization provided by models described under the first set.

Task II of the study involved 1-, 2-, and 3-dimensional experimental efforts to study bench-scale and intermediate-scale uncertainties associated with OIL sources. 1- and 2-dimensional experiments were conducted at University of Florida. These studies focussed on describing dissolution from multi-component OIL's at varying residual fluid saturations and distributions, and the characterization of OIL sources using partitioning and interfacial tracers. 1- and 3-dimensional OIL dissolution experiments were conducted at University of Florida, at Armstrong Laboratory at Tyndall Air Force Base, and in the field at Base Borden, Ontario, Canada.

Task III involved the application and the evaluation of stochastic models using data from the pilot-scale field sites located at Hill AFB, Columbus AFB, and Base Borden, Ontario, Canada. Data derived from partitioning/interfacial tracers and far-field dissolved OIL component distributions were used with the stochastic models to characterize OIL sources at each site in terms of the distribution and/or the moments of:

1) residual OIL and composition;
2) hydrogeochemical aquifer characteristics (i.e., sorption coefficients);
3) mass transfer coefficients for dissolution;
4) hydraulic conductivities; and
5) dissolved OIL component fluxes at an arbitrary source plane.

Support from this project has lead to 21 journal publications and facilitated the completion of six dissertations and two theses.

STOCHASTIC MODELING

Several stochastic modeling efforts were conducted during the course of this project as defined by Tasks I and III. These efforts were divided into three broad categories: the first set of models was developed to characterize the near-field region or source zone (contaminant source distribution and aquifer properties) using partitioning and/or interfacial tracer test results. The second set of inverse models was developed to make use of far-field aqueous phase contaminant concentration data to locate sources or define contaminant fluxes at arbitrary downstream source planes. The third set of models was developed to predict dissolution and far-field contaminant transport in heterogeneous groundwater systems given the aquifer and stochastic source zone characterization provided by the above-described models.

Ultimately, the intended application of the models developed herein was to used them as reconnaissance tools for ascertaining the location of ill-defined OIL sources, for characterizing OIL source morphology, and as predictive models. Thus, these models address the above-described second and third research objectives.

Source Characterization Modeling Using Tracer Data

Stochastic inverse methods were developed to quantify the spatial distribution of residual OIL saturations, hydraulic conductivities, hydraulic heads, and darcy fluxes using partitioning, interfacial and nonreactive tracer breakthrough curves. These methods assumed that the uncertainty in transport of a partitioning or interfacial tracer resulted from small-scale variations in a steady-state velocity field (due, in turn, to fluctuations in the hydraulic conductivity field) as well as spatial variations in OIL saturation. In contrast, uncertainty in the transport of non-partitioning tracers was due solely to the velocity variations. Thus a comparison of the arrival times for the reactive and non-reactive tracers at a particular sampling location provided a measure of the amount of residual OIL seen by the tracers along the flow path to that location. Two techniques were developed during the course of the investigation.

In the first technique, the traditional advective-disperse equation (ADE) was used to describe the transport of non-reactive and reactive tracers in the subsurface environment with the latter retarded as a result of the presence of OIL (Zhang, 1997). Using first-order perturbation techniques, a system of coupled transient second-order stochastic partial differential equations were derived to describe the temporal propagation of the first and second moments of the partitioning (or interfacial) and non-reactive tracers through the random pore water velocity and OIL fields. These equations were solved for the moments using a standard block-centered finite-difference approach. Once the unconditional spatial moments were determined, a distributed parameter Kalman filter was developed to condition the transient tracer distributions, and the steady-state pore-water velocity and OIL fields using transient, spatially distributed reactive and non-reactive tracer measurements.

Tests of the method using a synthetic data set showed that the algorithm provided three-dimensional optimal estimates of spatially-distributed OIL and hydraulic conductivity fields that captured dominant characteristics of the underlying random fields. Furthermore the algorithm accurately assessed the error in its predictions.

The second technique used temporal moment data that summarized tracer break-through at various spatial locations within the source zone, rather than transient tracer concentrations, to characterize the source region (James et al., 1996, 1997). This method assumed that the transport of temporal tracer moments through random pore water velocity and random OIL fields could be predicted using a steady-state advection-dispersion equation. Using first-order perturbation techniques a system of coupled steady-state second-order stochastic partial differential equations were derived to characterize the transport of the first and second stochastic moments of the temporal moments of the reactive and non-reactive tracers through random pore water velocity and OIL fields. The resulting system of elliptic equations was solved using a standard seven-point finite difference method. A steady-state Kalman filter (or simple co-kriging algorithm) was developed to condition the reactive and non-reactive temporal tracer moments, and the steady-state pore-water velocity and OIL fields using estimates of the reactive and non-reactive tracer temporal moments obtained from each measurement location. Tests of this method using a synthetic data set showed that this algorithm also successfully captured dominant features of the random OIL and pore water velocity distributions, and accurately predicted the uncertainty associated with its estimates.

The steady-state temporal moment-based optimal estimation algorithm avoided time and memory-consuming time-stepping, and thus was much more computationally efficient than

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the concentration-based optimal estimation algorithm. However, the temporal moment method required complete breakthrough curves at each measurement location, while the concentration method worked with sparse transient data. Both methods were applied to partitioning tracer data from the isolation test cell at Hill AFB (James et. al. 1996, 1997 and Zhang 1997).

In order to develop models to accurately account for the presence of injection and extraction wells, as well as anisotropic conductivity fields, a new numerical method was developed to approximate head and flux covariances in non-stationary flow fields (James and Graham, 1998). This numerical method used a mixed finite element method to solve a coupled system for the head and flux, combined with an adjoint sensitivity method to determine the head and flux covariances. Because the flux covariances were obtained directly from solution of the coupled system, the results obtained were more accurate than those obtained using a conventional finite difference or finite element approach. Use of this technique (as opposed to infinite domain or more conventional finite domain numerical approaches) allowed a more accurate determination of the covariances in a complex flow field such as in the isolation test cell at Hill AFB.

Source Characterization Modeling using Aqueous Phase Contaminant Concentrations

Two inverse models were developed to locate sources and to characterize contaminant fluxes at arbitrary control planes. These models used far-field contaminant concentration data to locate sources and define contaminant fluxes. One of the models used 'simulated annealing' to determine the location of contaminant sources and estimate contaminant fluxes based on aqueous-phase contaminant concentrations measured down gradient from the source. Simulated annealing is an optimization technique capable of minimizing func-

tions of a large number of variables. The annealing algorithm was used to minimize the sum of the squared deviations between measured aqueous phase concentrations and concentrations predicted with a three-dimensional transport model. The method of simulated annealing permits random movement away from local minimum in favor of movement towards a global minimum. The inverse model was used to obtain optimal estimates of OIL source locations. The model was validated using water quality data developed from several 3-dimensional laboratory transport experiments (Newman et al. 1996 and 1997a).

A second inverse model was developed which estimated contaminant fluxes from an arbitrary source plane located down gradient from a source (Hatfield and Stauffer 1996 and Hatfield, K. 1997a and b). This second model used 'Minimum Relative Entropy' (MRE) to characterize the contaminant sources in terms of random variables that define spatially variable contaminant fluxes over a source plane.

To explain MRE model and how it was applied consider what is illustrated in Figure 1, a hypothetical groundwater contaminant plume and the associated emissive source plane on the y-z coordinate field oriented perpendicular to the direction of groundwater flow. The source plane is shown subdivided into elements, where m_n is the contaminant flux over element n. Down-gradient from the source plane is dissolved contaminant concentration, c_j, observed at location, j. The transfer function, T_{jn}, represents the change in contaminant concentration at location, j, due to a unit change in source flux, m_n. The total concentration, c_j, is calculated from the products of elemental fluxes, m_n, and transfer functions, T_{jn}, summed over the source plane.

$$c_j = \sum_{n=1}^{N} T_{jn} m_n \qquad (1)$$

Groundwater

m_n = source

d_j = dissolved phase concentration at location $j(x,y,z)$

+j

x

z

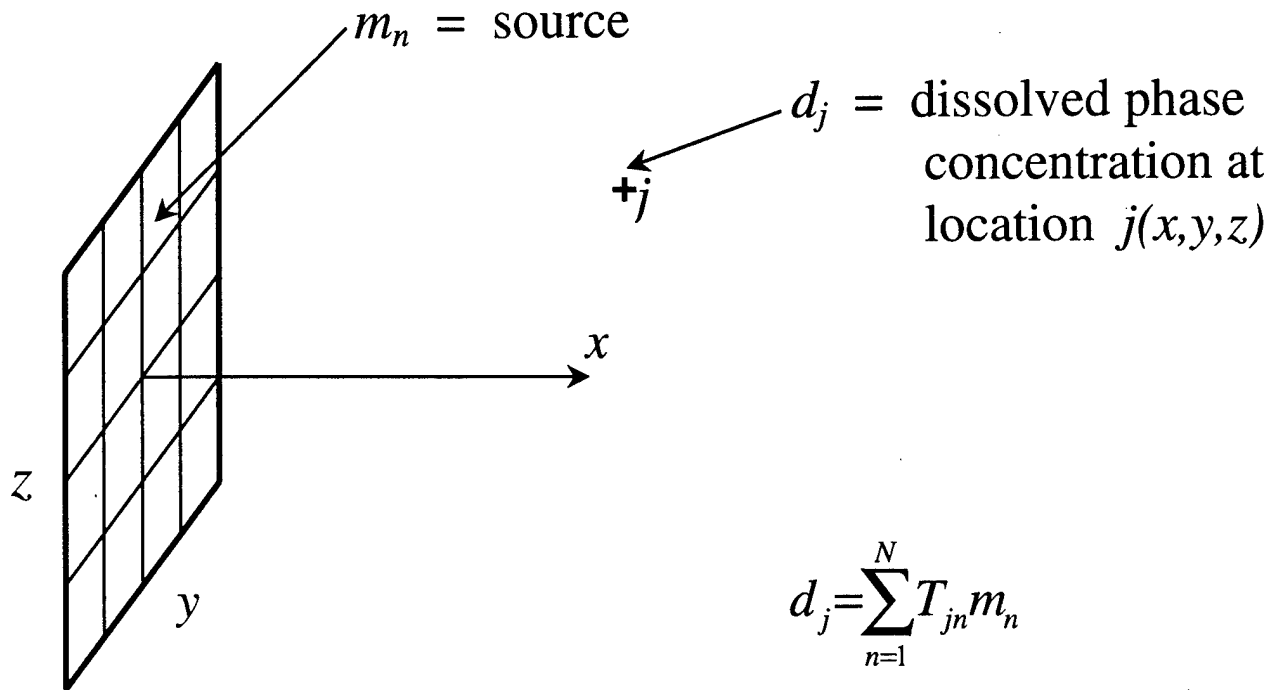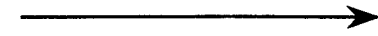y

$$d_j = \sum_{n=1}^{N} T_{jn} m_n$$

Figure 1: Conceptual source plane model

For the inverse problem it was assumed that transfer function, T_{jn}, was known for all combinations of j (= 1, 2,...,k) and n (= 1, 2,..., N), and that contaminant concentrations were known at k sampling locations where k < N. Thus, the inverse problem was to determine what values for all m_n, that best characterize the elemental source flux distribution across the source plane and reproduce down-gradient plume concentrations, c_j, for all values of j.

The following general procedure for solving the inverse problem was formulated:

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Step 1: Recast the deterministic relationship between unknown elemental contaminant fluxes at the source plane and down-gradient contaminant concentrations into a stochastic problem. Thus, the expected value of the contaminant concentration c_j, are expressed as a function of the probability density function of elemental contaminant fluxes, m_n or $q(m_n)$.

$$\bar{c}_j = \int_M q(m) \left[\sum_{n=0}^{N} T_{jn} m_n \right] dm \qquad (2)$$

Step 2: Assume a uniform probability density function $p(m_n)$, as a prior estimate of $q(m_n)$.

Step 3: Apply the Theory of Minimum Relative Entropy and derive $q(m_n)$, using available observations of down-gradient concentrations, c_j.

Step 4: With $q(m_n)$ found for each source plane element, calculate the expected values for these fluxes, m_n.

$$\hat{m}_n = \int_M q(m_n) m_n dm_n \qquad (3)$$

Once values of all the elemental m_n's are known, the forward problem is examined; which is to quantify the elemental flux estimation error and determine how the uncertainty in the estimated values of elemental fluxes, m_n, are manifested in estimated plume concentrations at unsampled locations. A general procedure for solving the forward problem was formulated as follows:

Step 1: With $q(m_n)$ found for each source plane element, calculate the expected values of the elemental source plane fluxes, m_n

Step 2: Using the expected element fluxes, calculate the expected concentrations directly through the transfer function, T_{jn}.

Step 3: Using $q(m_n)$, and the Monte Carlo simulation method, obtain estimates of down-gradient contaminant prediction errors. These are errors due to uncertainties in estimated elemental source fluxes.

To test the MRE inverse model, data from a 3-dimensional transport experiment were used (Hayworth et al. 1997 and Newman et al. 1997a). The data comprised of concentra-

tions of three non-reactive tracers (chloride, sulfate, and bromide) measured from plumes generated from three separate, continuous point sources located within a 3-dimensional flow field. Steady-state aqueous phase concentrations were measured down-gradient from the sources for use with the MRE inverse model. Result of the inverse modeling produced both the expected values of dissolved chloride, sulfate, and bromide fluxes and the corresponding probability density functions needed to characterize flux uncertainty. These probability density functions were subsequently used in Monte Carlo simulations to quantify contaminant prediction errors due to the ill-defined sources (Newman et al., 1997a and Hatfield and Stauffer 1996).

Far-field Contaminant Transport Modeling Using Stochastic Source Zones

A third set of models was developed to predict dissolution and far-field contaminant transport in heterogeneous groundwater systems given the stochastic source zone and aquifer characterization provided by the optimal estimation algorithms described above. In the first set of models an Eulerian perturbation approach was used to predict the mean macro-dispersive flux and variance of a contaminant plume released from a subsurface source region (Li, 1998; Li and Graham 1998a,b). In the second set of models, a Lagrangian stochastic-advective approach was used to used to predict the mean and covariance of contaminant release from source regions and the subsequent expected value and variance of mass flux past downstream compliance boundaries (Demmy et al, 1998b).

Eulerian Approach

In the first phase of this work approximate unconditional moment equations for a concentration plume in a two-dimensional spatially random transmissivity field subject to spatially random recharge and nonuniform (linear trending) velocity were derived and solved (Li

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and Graham, 1998a). Closed-form expressions were derived for the unconditional, non-stationary auto-covariances for head and velocity, and the cross-covariances between velocity, head, recharge, and log-transmissivity based on a system of coupled first-order partial differential moment equations and assumed hole-type input covariance functions for log-transmissivity and recharge. The unconditional flow related moment equations were incorporated into a system of solute transport moment equations which was solved using a Galerkin finite element algorithm. Results showed that a constant positive mean recharge produced a mean velocity gradient that increased ensemble mean plume spreading in the longitudinal direction. Spatial variability in recharge further enhanced the spreading of the ensemble mean plume, especially in the lateral direction. Uncertainty in the spatial distribution of recharge also increased the extent of the ensemble standard deviation plume, particularly in the lateral direction, and increased the coefficient of variation of solute concentration. The uncertainty in the prediction of solute transport increased with increasing recharge variance and spatial correlation scale.

In the second phase of this work the approach described above was extended to predict the unconditional moments of head, velocity, and concentration under transient flow conditions, which were assumed to be caused by a spatio-temporally random recharge (Li and Graham 1998b). Semi-analytical solutions were derived for the unconditional covariances for transient velocity with a constant mean recharge using a Fourier transform approach. Results demonstrated that the velocity covariance derived for the steady-state random recharge field was a limiting case of the spatio-temporally variable velocity covariance with an infinite temporal correlation scale. Another limiting case indicated that introduction of temporally variable but spatially uniform recharge had no effect on the velocity covari-

ances, and thus no effect on the ensemble mean concentration plume spreading or the concentration prediction uncertainty. The equations for mean concentration and macrodispersive flux under zero mean transient recharge were decoupled in the Laplace-Fourier domain and solved using a fast Fourier transform algorithm, which significantly reduced the computational demand. The first-order concentration variance was solved using three different approximate techniques: an approximate fast Fourier transform technique, a finite element method, and a direct numerical integration. The simulation results showed that introduction of a spatio-temporally-random recharge enhanced both longitudinal and lateral mean concentration plume spreading compared to the no recharge case. However, transient recharge produced less spreading and less concentration prediction uncertainty than the steady-state spatially random recharge case.

In the final phase of this work the joint effects of uncertain contaminant source and random velocity fields on the evolution of concentration moments were examined (Li 1998). The continuous mass-release rate in a contaminant source zone was assumed to be a random field that could be correlated or uncorrelated with the random velocity field. Steady-state unconditional velocity and mass release rate covariances were incorporated into concentration moment equations that were solved using fast Fourier transform techniques. The results showed that whether correlated or uncorrelated with local velocity, an uncertain mass release rate had little impact the ensemble mean concentration plume spreading. A new term, the covariance between random mass release rate and concentration, was introduced in this work to characterize the correlation between mass release rate in the source zone and concentration throughout the domain. This term served to transfer the mass release rate uncertainty to the concentration prediction uncertainty, and quantified

the information that local resident concentrations contain regarding source strength throughout the source region. Results showed that a mass release rate that was correlated with local velocity would cause higher concentration prediction uncertainty than an uncorrelated mass release rate, especially for a larger source area. However a mass release rate that was correlated with the local velocity was also more strongly correlated with downstream solute concentrations than the uncorrelated case, indicating more opportunity for reducing prediction uncertainty by conditioning with site-specific data. The extent of the source area in the direction of flow was found to have an important effect on the magnitude and extent of the ensemble concentration moments but no effect on their rate of spreading.

Lagrangain Approach

In the second approach a Lagrangian stochastic-advective approach was used to predict the mean and covariance of contaminant release from source regions and the subsequent expected value and variance of mass flux past downstream compliance boundaries (Demmy at al, 1998a). In the context of this work, a contaminant source would release solutes into the groundwater. Of interest was the subsequent transport of these solutes through the subsurface. Formulating this problem as mathematical equations, the contaminant source could be thought of as a boundary condition for the equation that models solute transport. Traditionally, much attention has been focused upon the governing equations, with the boundary conditions being known. However, these sources could be reasonably expected to be quite heterogeneous, and thus the boundary conditions describing the introduction of the contaminant into the subsurface deserve investigation.

Levenspiel and Turner (1970) identified two different modes for introducing contaminant into the subsurface: a resident injection mode in which solute was delivered to some given volume of fluid, and injection in flux where solute was delivered in an influent fluid. Kreft and Zuber (1978) examined these injection modes in context of the advection-dispersion equation. However, it has been shown that the advection-dispersion equation with constant coefficients generally is inadequate to model solute transport in heterogeneous aquifer over different spatial scales (Dagan, 1989; Gelhar, 1993). In order to elucidate the effect of injection mode upon solute transport in heterogenous aquifers, a stochastic-advective approach was adopted in which large-scale heterogeneities in the flow field were assumed to dominate the plume-scale transport processes for non-reactive solutes. A three-dimensional heterogeneous aquifer was considered in which the groundwater flow was assumed steady, incompressible, and irrotational. As such, this flow field may be conceived of as a collection of streamtubes. Without loss of generality, the streamtube model implied by Dagan's (1984) formulation was adopted in which each streamtube carries some equal volumetric weight at some definition location. To simplify the conceptual model, all streamtubes were assumed to have the same cross-sectional area in the injection plane orthogonal to the mean flow direction. Placing an equal mass into each streamtube corresponds to a uniform resident injection mode, whereas placing a mass proportional to the local pore water velocity into each streamtube corresponds to injection in fluid flux. The effects of these different injection modes were examined through numerical experimentation. An implementation of the turning bands method generated an exponentially correlated isotropic log saturated hydraulic conductivity field 12 correlation lengths in the mean flow direction x by 8 correlation lengths in the y and z directions, with five conduc-

tivity blocks per correlation length (Tompson et al., 1989). Constant head boundaries were specified at the y-z boundary planes. No flow boundaries were specified at the x-y and x-z boundary planes. A mixed finite element scheme was used to generate a system of coupled pressure-velocity equations (James and Graham, 1998). Solution of these equations resulted in a set of velocities for input into a particle tracking scheme.

One particle was introduced into each velocity field realization at a distance of two correlation lengths from the upstream y-z plane and equidistant from extreme x-y and x-z domain boundaries. An adaptation of Pollock's (1988) semi-analytical method yielded local velocities, particle trajectories, and travel times across elements. Ensemble statistics for velocity fields associated with log conductivity variances of 0.1, 0.5, and 1.0 were calculated from data collected from 4000 statistically independent particle trajectories for each log conductivity value.

Results of the numerical experiments showed that the mean arrival time for uniform resident injection is a non-linear function of position. This apparent non-stationarity for the uniform injection mode was predicted by Dagan et al. (1992), in that two regimes were identified: one in which the mean arrival time propagated as:

$$\bar{t} = \frac{x}{v_h} \tag{4}$$

in which x was distance and v_h was the harmonic mean velocity under the "small x-a approximation," and one in which the mean time propagated as x/arithmetic mean velocity under the "large x approximation." The transition between these two regions of approximation discussed was in the context of two-dimensional heterogeneous aquifers by Cvetkovic et al. (1996) and in the context of two-dimensional heterogeneous soils by

Vanderborght (1997). Results of the numerical experiments also showed that injection in flux results in a linear propagation of mean mass arrival time. The mass arrival time variance for both uniform and flux injection is a non-linear function of distance from the injection plane, but the arrival time variance is lower for the injection in flux and appears to reach a linear regime more rapidly than the uniform resident injection case.

LABORATORY INVESTIGATIONS

Laboratory investigations under Task II included 1-dimensional column and 2-dimensional box experiments conducted at University of Florida and 3-dimensional model aquifer experiments conducted at Tyndall Air Force Base. These experiments were designed to show how variations in source morphology impact variations in aqueous phase concentrations and fluxes over time and space occurring in both the OIL source region and in regions down gradient within the contaminant plume (i.e., the first research objective).

1-D Column Experiments

Column experiments were conducted using various surfactants to measure the interfacial area between OIL and water and air and water in porous media (Saripalli et al., 1997, 1998a, 1998b, and Kim et al., 1997, 1998). This information could be used to obtain a more complete description of the OIL morphology in porous media and predict the transport of chemical in the presence of fluid interfaces. OIL morphology was investigated for both trapped and continuous OIL phases. Columns with capillary barriers were constructed to control the capillary pressure and experiments were conducted at different steady-state water flow rates to produce a range of OIL saturations. The interfacial tracers were then used to investigate changes in interfacial area with OIL phase saturation

(Saripalli et al., 1998b). Column experiments were also conducted in which the trapped OIL saturation was changed by reducing interfacial tension between OIL and water; this was achieved by changing surfactant concentration and salinity in the mobile aqueous phase. These experiments were designed to look at OIL morphology expected during OIL dissolution or mobilization as a result of interfacial tension reduction (Saripalli et al., 1997). Finally, PCE contaminated sand column experiments were conducted at different flow rates to investigate the utility of tracers as source characterization tools under non-equilibrium transport conditions (Kim 1998).

To facilitate the analysis of the 1-dimensional experimental results, several new methods were developed for analyzing column breakthrough curves depicting eluted dissolve OIL or tracer concentrations over time. One method was developed for analyzing break-through data with serious data collection gaps (Helms, et al. 1995 and 1998a and Hatfield, K. 1996). Field and laboratory experiments are often conducted with the intent of col-lecting data over time. Unfortunately, data collection gaps often occur either at the beginning of an experiment (i.e., when data collection efforts do not begin soon enough to capture early time results) or near the end of an experiment (i.e., when data collection stops prematurely). These gaps can complicate the interpretation of transient phenomena reflected in an existing data set. Several numerical methods have been developed to esti-mate missing experimental results regardless of whether results are missing at the begin-ning or at the end of an experiment. In addition, an analytical method has been devised for temporal moment analysis using truncated data sets (i.e., data sets missing results from the end of an experiment). For this project both methods were used to estimate temporal

moments and to ascertain parameters pertinent to field- and laboratory-scale contaminant transport (i.e., dispersion coefficients, retardation factors, pore-water velocities, etc.).

To analyze multi-modal breakthrough curves, a new semi-analytical temporal moment method was developed (Helms et al., 1998b). The method was derived on the assumption that multiple convective-dispersive transport equations may be superimposed to approximate multi-modal breakthrough curves. Analytical moment equations were derived and then demonstrated to be quite robust and be capable of accurately estimating the error in predicted moments with noisy and truncated data sets. Both the multi-modal method and the above-described method for simple truncated breakthrough curves were used to estimate temporal moments of partitioning tracers monitored in a field test cell at Hill AFB. These tracer moments were later used in the stochastic inverse modeling detailed above (James et al., 1996 and 1997) to estimate 3-dimensional hydraulic conductivities, OIL distributions and saturations within the Hill AFB test cell.

2-D Model Aquifer Experiments

Two dimensional laboratory experiments were conducted to evaluate the use of partitioning tracers as tools for quantifying 2-D OIL source morphology. These experiments were conducted with clean sand, or aquifer material from a field site at Hill AFB and OIL (PCE or LNAPL from Hill AFB) to generate OIL sources of known morphologies within 2-D flow systems. For these experiments, either PCE was directly injected into water-saturated sand packed systems to create regions of porous media at residual OIL saturation, or contaminated sand was packed as a rectangular source region surrounded by uncontaminated sand to create a 2-D flow through system. Partitioning tracers were then used to quantify OIL mass and provide a measure of OIL distribution within the system

(Jawitz et al., 1998b,c and Jawitz 1999). To allow collection and measurement of flow and flux averaged concentrations of OIL constituents and tracers (i.e., partitioning, interfacial and nonreactive) a special 2-D laboratory model was constructed with a segmented extraction well. This system design was used to further investigate dissolution and partitioning tracer behavior in non-uniformly distributed OIL systems. Finally, a new system was developed for automated sampling and analysis of effluent samples from column and 2-D box experiments. The new system provided superior control over manual methods and ran unattended for the complete breakthrough period. This method was used for conducting partitioning tracer tests, dissolution experiments, and remediation evaluations (Jawitz 1995 and Jawitz et al., 1998a).

3-D Model Aquifer Experiments

Since June 1995, the University of Florida research team has been collaborating with Drs. Tom Stauffer and Joel Hayworth of Armstrong Laboratory, Tyndall AFB, FL. Research efforts have included several experimental investigations of 3-dimensional OIL transport in a large 2.0 m x 1.7 m x 0.5 m model aquifer at Tyndall Air Force Base and the development of two numerical inverse models.

As part of Task II, a large 3-dimensional model aquifer was constructed to simulate a phreatic aquifer. The system was specifically designed for use with chlorinated solvents (i.e., all wetted surfaces are nonsorptive; system is completely enclosed, allowing mass-balance of volatile components). In order to obtain aqueous phase samples from within the porous medium multi-port samplers were fabricated. The model aquifer system was designed for multiple experiments each with a different porous media and sample port

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configuration. The current system was packed with clean, medium grained sand and equipped with 500 sampling ports.

A series of experiments were initially performed to characterize the hydrodynamics of the 3-D system (i.e., define longitudinal and transverse dispersivities) [Newman et al. 1998]. Plumes were developed from a continuous plane source located below the phreatic surface using chloride as a nonreactive tracer. Transient breakthrough concentrations and steady-state, transverse concentration distributions were measured at three locations along the midline of the source. A Levenberg-Marquardt nonlinear, parameter estimation algorithm was used to fit an analytical three-dimensional transport model to the experimental data. The steady state, transverse concentration distributions were used to estimate the transverse dispersivities. The transient, breakthrough concentrations were used to estimate the longitudinal dispersivity. The characterization experiments were completed.

Following the hydrodynamic characterization of the 3-D aquifer model system, a 3-D source uncertainty experiment was conducted. In this experiment three non-reactive tracers (chloride, sulfate, and bromide) were injected beneath the phreatic surface of the model aquifer from three separate continuous point sources of fixed strength and known position [Newman et al. 1996, 1998]. After the system achieved steady-state, aqueous tracer concentrations were measured down gradient from the sources. Measured tracer concentrations were then used to validate two new numerical inverse model capable of locating contaminant sources using dissolved source constituent concentrations measured down gradient from a source (the above-described model based on minimum relative entropy and the analytically base model using simulated annealing). The model validation

studies demonstrated that both inverse models were successful in locating the all point sources with a high degree of accuracy.

Several OIL source dissolution experiments were then conducted. During an initial experiment ten residual OIL phase sources were created inside the 3-D model aquifer. These sources contained a neutrally buoyant liquid volume mixture of 55% n-hexadecane, 25% trichloroethylene (TCE), and 20% tetrachloroethene (PCE); the OIL mixture was also dyed with an organic dye, red-o. Because TCE and PCE are relatively soluble in water when compared to hexadecane they behaved as the experimental contaminants. Aqueous phase concentrations of PCE and TCE were monitored at 500 sample ports bi-weekly for several weeks. Once the plume achieved pseudo-steady-state, a partitioning tracer experiment was performed. A pulse of partitioning tracers consisting of: methanol, hexanol, 2,2-dimethyl-3-pentanol, 6-methyl-2-heptanol, and bromide (a non-reactive tracer), was introduced into the flow-through system. The aqueous phase tracer concentrations were measured down gradient from the OIL sources. The partitioning tracer breakthrough data were used to estimate the mass of OIL in the system and to indicate the relative source location.

Once OIL source dissolution experiment was complete, the 10 OIL sources were excavated. Because red-o dye was mixed in with the OIL sources it was possible during excavation to delineate and record through digital photographs, the location and the spatial geometry of the OIL sources. Results from the three-dimensional DNAPL dissolution experiments were used to validate predictions generated from various stochastic/deterministic inverse models Newman (1999).

3-D Field Experiments

A 3-dimensional field experiment was conducted in a isolation cylinder at Base Borden, Ontario Canada to assess the effectiveness of partitioning tracers and inverse models as tools for delineating the morphology of a groundwater contaminant sources. The theory of using partitioning tracers to quantifying OIL saturation and mass was reviewed by Jin *et al.* (1995) and Annable *et al.*, (1998).

This study began with an initial partitioning tracer test to characterize background sorption and dissolved phase hydrodynamic transport conditions inside a steel isolation cylinder that was driven into the Borden Aquifer. Following the initial partitioning tracer test two liters of pure PCE was injected into the steel cylinder to create a PCE source of known mass. Once the residual source was created, a partitioning tracer test was performed to define the source morphology inside the cylinder.

The isolation cylinder was essentially a steel cylinder of 0.76-m diameter driven 2.5 m into the Borden Aquifer and keyed about 0.25 m into the aquitard (Figure 2). The exact depth to the aquitard was determined by collecting a soil core before the cylinder was installed. The components comprising the injection/extraction system and the sampling system were inserted horizontally through the cylinder walls to minimize the disturbance of the soil column. To install these components, the perimeter around the cylinder was excavated. A sheetpile cell of 2m x 2m was constructed around the in-situ column to facilitate excavation.

The injection/extraction system consisted of two 6" stainless drive point piezometers (1.25" O.D.) connected to Teflon tubing. These drive points were inserted through holes
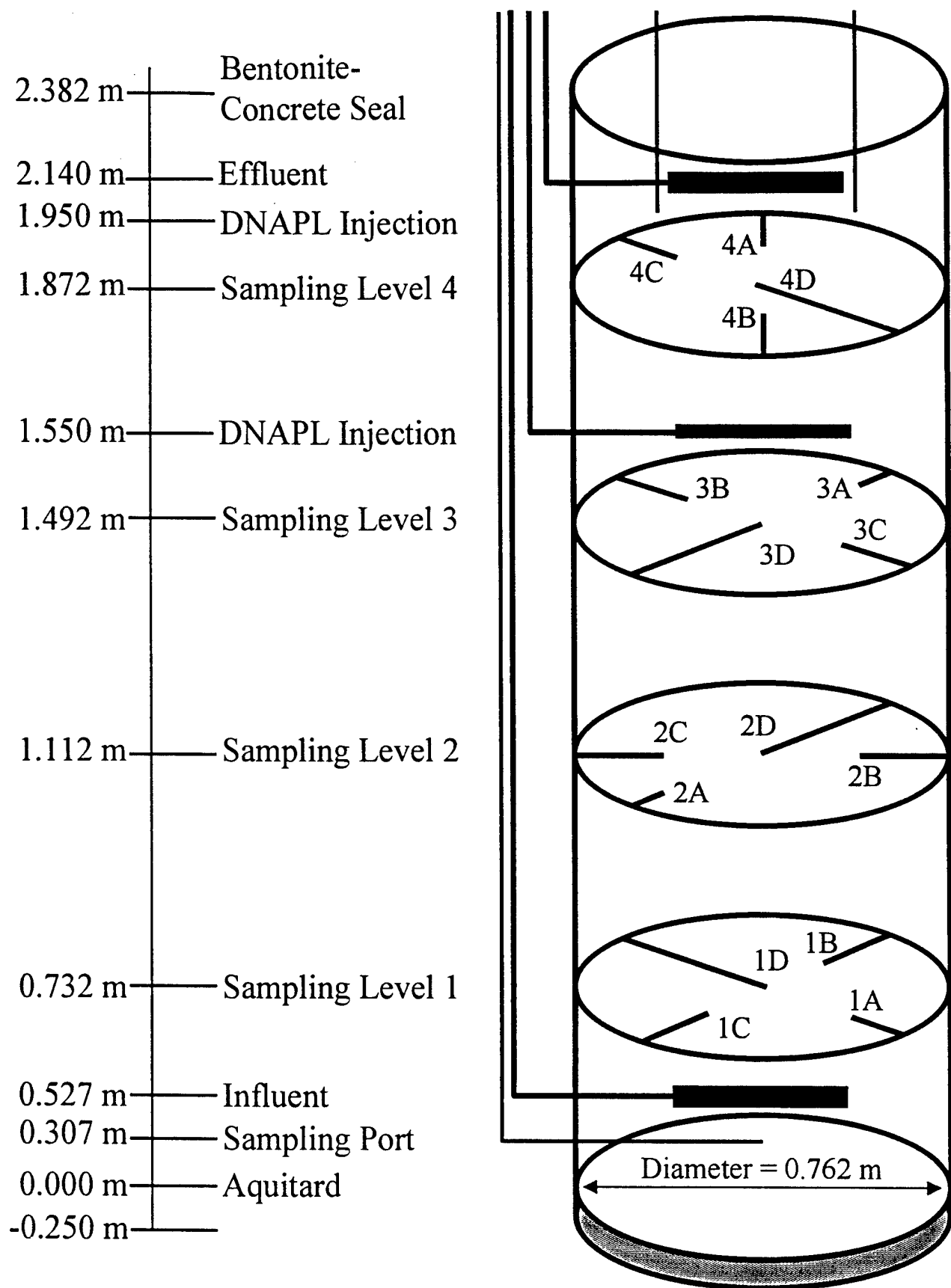
Depth	Label
2.382 m	Bentonite-Concrete Seal
2.140 m	Effluent
1.950 m	DNAPL Injection
1.872 m	Sampling Level 4
1.550 m	DNAPL Injection
1.492 m	Sampling Level 3
1.112 m	Sampling Level 2
0.732 m	Sampling Level 1
0.527 m	Influent
0.307 m	Sampling Port
0.000 m	Aquitard
-0.250 m	

Diameter = 0.762 m

Figure 2. Isolation Cylinder.

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cut in the cylinder walls and then gently pushed horizontally into the soil column. Twenty 1/8" stainless steel monitoring ports were located at five different depths; thus, there were four sampling ports per depth situated around the column. To install these samplers, a regular steel casing (5/16" O.D. 0.018" wall thickness) was first driven with a disposable stainless steel driving point, the port was then inserted inside the casing and the casing was carefully pulled out. In the same fashion, three PCE injection ports (1/8" stainless steel tube perforated over 200 mm of length and wrapped by stainless steel screen) were installed, one the middle of the column and two 6" below the extraction port. Sampling ports were properly sealed and swagelock fittings were used to install the 1/8" stainless steel tubes. For the injection/extraction system 1/4" pipe and swagelock fittings were used. The top of the cylinder was sealed allowing the system to flow under pressure. The seal consisted of one inch of bentonite and 11" of concrete.

An initial tracer test was conducted with the nonreactive tracers potassium bromide and methanol, in conjunction with partitioning tracers 2,3-dimethyl-2-butanol, 2,4 -dimethyl-3-pentanol, and 2-ethyl-1-hexanol. Approximately 20 liters (0.07 pore volume) of the tracer mixture was introduced over 1.85 hours after a steady flow of 0.184 l/min had been established in the cylinder. Once the tracer mixture was introduced, the flowrate was maintained for 2.3 days (~ 2 pore volumes). For the duration of the tracer experiment, water samples were collected at each of the 20 sampling ports and at the extraction well.

Following the first tracer test, pure PCE was injected into the isolation cylinder through the three available PCE injection ports. Based upon an estimated pore volume of 350 liters for the isolation cylinder, 2 liters of PCE were injected to create a source zone having a column-wise residual of 0.6 percent OIL. Once the PCE source was created, a second

tracer test was conducted. This test was conducted in the same manner as described above except for two modifications. First, the flowrate was increased to 0.4 l/min (~ 2 pore volumes per day). Second, approximately 40 liters (0.14 pore volume) of tracer solution was introduced over 1.85 hours. The duration of the experiment was 5.5 days (11.0 pore volumes). The second tracer test was conducted to verify the mass of PCE in the cylinder and determine the residual PCE distribution in space (i.e., the source morphology).

Results from the initial tracer test indicated that non-partitioning and partitioning tracers all exhibited approximately the same travel time through the column. This indicated that there was no background sorption of the partitioning tracers (Figure 3). Results from the post-spill tracer test showed separation breakthrough curves, indicating variable tracer residence times caused by partitioning into OIL phase (Figure 4).

Because mass of residual PCE in the isolation cylinder changed during the experiment (due to NAPL dissolution) is was necessary to develop and test new temporal moment expressions to characterize tracer behavior under dissolving OIL conditions (the typical field situation). Application of these methods to data collected from the Borden experiment, lead to correct interpretations of partitioning tracer behavior and subsequent accurate estimation of OIL mass in the isolation cylinder. Whereas use of previously developed methods from Jin et al. (1995) for fixed OIL phases lead to low estimates of OIL mass (Newman 1997b). Results from the Borden experiment represent the first field validation of partitioning tracers.
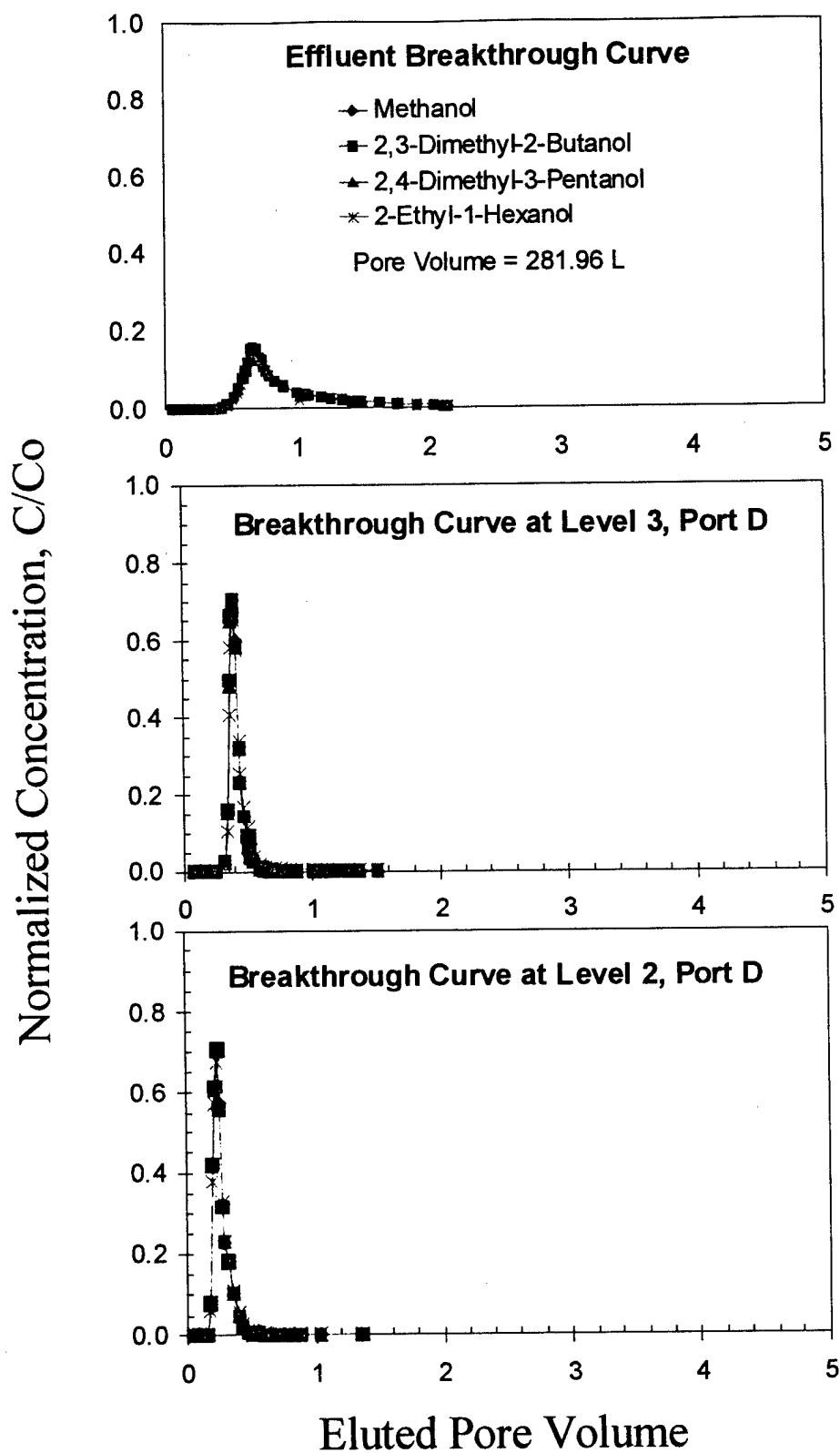
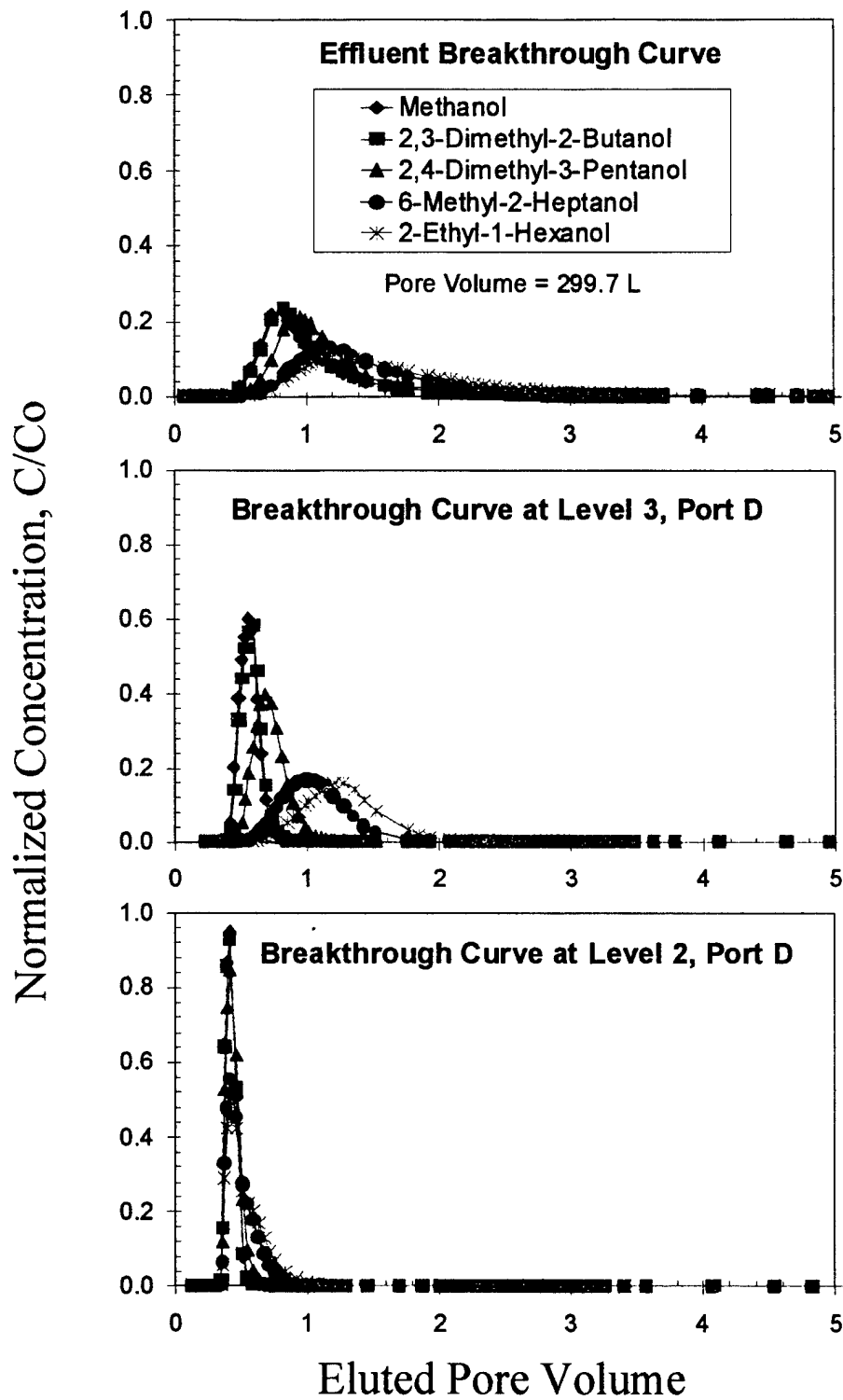Figure 3. Breakthrough curves for initial tracer test.

Figure 4. Breakthrough curves for post-spill tracer test.

PUBLICATIONS AND DISCLOSURES

Journal Publications (a Total of 21)

The following are refereed journal publications derived from project supported research.

Annable, M.D., P.S.C. Rao, K. Hatfield, W.D. Graham, and A.L. Wood. 1998.

Burris, D. R., K. Hatfield, and N.L. Wolfe. 1996.

Burris, D.R., C.A. Delcomyn, B. Deng, L.E. Buck, and K. Hatfield. 1998.

Demmy, G.G., S. Berglund, and W. D. Graham. 1998b.

Hatfield, K., D. R. Burris, and N.L. Wolfe. 1996

Helms, A.D., K. Hatfield, and W. Graham. 1998a.

Helms, A.D., K. Hatfield, M.D. Annable, P.S.C. Rao, W. Graham., and A.L. Wood. 1998b.

James, A.I., W.D. Graham, K. Hatfield, P.S.C. Rao, and M.D. Annable. 1996.

James, A.I., W.D. Graham, K. Hatfield, P.S.C. Rao, and M.D. Annable. 1997.

James A.I., and W.D. Graham. 1998.

Jawitz, J.W., M.D. Annable, and P.S.C. Rao 1998a.

Kim, H., P.S.C. Rao, M.D. Annable. (1997).

Kim, H., M.D. Annable, and P.S.C. Rao. (1998).

Li, L. and W.D. Graham. 1998a.

Li, L. and W.D. Graham. 1998b.

Newman, M.A., J.S. Hayworth, K. Hatfield, and T. Stauffer 1998.

Rao, P.S.C., M.D. Annable, R.K. Sillan, D. Dai, K. Hatfield, W.D. Graham, A.L. Wood, and C.G. Endfield. 1997.

Saripalli, K.P., Annable, M.D., and Rao, P.S.C., and Annable, M.D. (1997).

Saripalli, K.P., Rao, P.S.C., and Annable, M.D. (1998a).

Saripalli, K.P., M.D. Annable, P. S. C. Rao. (1998b).

Sillan, R.K., M.D. Annable, P.S.C. Rao, D. Dai, K. Hatfield, W.D. Graham, A.L. Wood, and C.G. Enfield. 1988.

Dissertations and Theses Supported

The following are dissertations and theses supported by the project.

Demmy, G. 1999.

Helms, A. 1996.

Jawitz, J.W. 1995.

Jawitz, J.W. 1999.

Kim, Hoenki. 1998.

Li, L. 1998.

Newman, M.A. 1999.

Zhang, Yan. (1997).

Interactions/Conferences (a total of 14)

The following are conferences where grant support research was presented.

Demmy, G.G., K. Hatfield, and T.B. Stauffer, 1998a.

Hatfield, K. 1996.

Hatfield, K. and T.B. Stauffer. 1996.

Hatfield, K. 1997a.

Hatfield, K. 1997b.

Hayworth, J.S., T.B. Stauffer, and K. Hatfield. 1997.

Helms, A., C. Bagget, K. Hatfield, and P.S.C. Rao. 1995.

James, A.I., W.D. Graham, K. Hatfield, P.S.C. Rao, and M.D. Annable. 1996.

Jawitz, J.W., M.D. Annable, and P.S.C. Rao. 1998b.

Jawitz, J.W., Annable, M.D., and Rao, P.S.C. 1998c.

McDonough, C.B., K. Hatfield, T.B. Stauffer, and L.E. Libelo, 1997.

Newman, M.A., J. Hayworth, K. Hatfield, and T. Stauffer. (1996).

Newman, M.A., K. Hatfield, J. Hayworth, and T. Stauffer. (1997a).

Newman, M.A., B.J. Megic, J.W. Jawitz, K. Hatfield, J.A. Cherry, M.D. Annable, P.S.C. Rao, and D. Smyth, (1997b).

New Discoveries/Inventions/Patent disclosures

None.

Honors/Awards

None.

INTERACTIONS/COLLABORATIONS AND PERSONNEL SUPPORTED

Interactions/Collaborations

University of Florida investigators collaborated with Air Force researchers Drs. Tom Stauffer and Joel Hayworth to conduct 1- and 3-dimensional experiments on dense non-aqueous phase liquid dissolution. This collaborative effort involved graduate students from the University of Florida's hydrology program that conducted experiments over the last three years at Armstrong Laboratory, Tyndall Air Force Base, Florida.

University of Florida investigators also collaborated with Dr. John Cherry of the University of Waterloo, Waterloo, Ontario, Canada. Experiments were conducted at Borden Air Force Base, Canada, to validate the utility of partitioning and interfacial tracers as tools to characterize OIL sources in the field.

Personnel Supported

University of Florida Faculty:

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> Jinhua Zhong (Ph.D.)

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